

PROCESS FOR DECREASING CONTENT OF PARTICULATE MATERIAL
CONTAINED IN EXHAUST GAS FROM LEAN BURN ENGINE OR THE LIKE

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to a process for decreasing the content of a particulate material contained in an exhaust gas from a lean burn engine or the like.

It is known that this type of the particulate material has a double-layer structure comprising a carbon solid fraction (soot) and a soluble organic fraction (SOF) covering the carbon solid fraction.

DESCRIPTION OF THE RELATED ART

There is a conventionally known process for decreasing the content of a particulate material contained in an exhaust gas, for example, from a diesel engine or the like, in which a ceramic filter (diesel particulate filter) is placed into an exhaust pipe to collect the particulate material in the filter, and when an amount of the particulate material collected reaches a predetermined value, the temperature of the exhaust gas is raised by an engine control, thereby burning the particulate material.

However, the conventionally known process has the following problems: an exhausting resistance is increased by the ceramic filter, and hence an engine output cannot be sufficiently utilized; the engine control for raising the temperature of the exhaust gas is complicated; and the filter temperature may exceed 1,000°C in some cases during burning of the particulate material, resulting

in damage to the ceramic filter.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a process for decreasing the content of a particulate material, which is capable of continuously converting the particulate material by the oxidization thereof to remarkably decrease the content thereof, and of suppressing an increase in exhausting resistance to a low level.

To achieve the above object, according to the present invention, there is provided a process for decreasing the content of a particulate material contained in an exhaust gas from a lean burn engine, comprising the steps of: generating plasma in the exhaust gas discharged from the lean burn engine and containing the particulate material, to thereby produce a plurality of $O(^1D)$ radicals and subsequently produce a plurality of per-hydroxide excited species; and oxidizing the particulate material by the per-hydroxide excited species.

When the plasma is generated in the exhaust gas, the following process is provided: $O(^1D)$ radicals and ozone excited species are produced by the collision between electrons released from electrodes and oxygen molecules \rightarrow hydroxide excited species are produced by the reaction of $O(^1D)$ radicals and ozone excited species with water \rightarrow per-hydroxide excited species HOO^* having a strong oxidizing force are produced by the reaction of the hydroxide excited species with oxygen. The production of the

per-hydroxide excited species is carried out independent of the temperature of the exhaust gas. The particulate material is oxidized and converted by the per-hydroxide excited species. The conversion of the particulate material by the oxidization is conducted continuously and at a relatively low temperature.

A plasma generating device has a good gas permeability, as compared with a filter, so that even if the plasma generating device is incorporated in an exhaust pipe, an increase in exhausting resistance is suppressed to a low level. Therefore, an influence cannot be exerted to an engine output.

If an intensity E of electric field is set at a value equal to or larger than 3.0 kV/mm and a power density Dw is set at a value equal to or larger than 1 W/cm³ in the plasma generating conditions, the amount of released high-energy electrons existing in the plasma is increased, and hence the production of the per-hydroxide excited species is efficiently conducted, whereby the conversion of the particulate material by the oxidization can be enhanced. However, if at least one of requirements of $E \geq 3.0$ kV/mm and $Dw \geq 1$ W/cm³ is lacked, the above-described effect cannot be obtained.

Further, if the surface of at least one of opposed electrodes which is opposed to the other electrodes is covered with a dielectric, the entire surface of the dielectric is uniformly charged upon application of a voltage. Therefore, the entire space between the dielectric and the other electrode opposed to the dielectric constitutes a plasma space, so that the frequency

of random contact between the particulate material and the per-hydroxide excited species can be increased to enhance the conversion of the particulate material by the oxidization. If opposed surfaces of the opposed electrodes are covered with dielectrics, respectively, an increase in the applied voltage is provided by an increase in impedance, but it is possible to provide a converting performance equivalent to that in the case where the one surface is covered, by setting the plasma generating conditions as described above.

According to the present invention, there is also provided a process for decreasing the content of a particulate material contained in an exhaust gas from a lean burn engine or the like and comprising a carbon solid fraction and a soluble organic fraction covering the carbon solid fraction, the process comprising the steps of: subjecting the soluble organic fraction to the reaction with oxygen under the presence of a catalyst to oxidize the soluble organic fraction; generating plasma in the exhaust gas to produce plasma excited species; and oxidizing the carbon solid fraction by the plasma excited species.

The soluble organic fraction usually comprises a polycyclic aromatic hydrocarbon and the like. A large amount of oxygen is contained in the exhaust gas from the lean burn engine. Therefore, if the catalyst is present, oxygen and the soluble organic fraction are brought into contact with each other on the catalyst, whereby the soluble organic fraction is oxidized and removed. This reaction occurs even at a low temperature.

When the plasma is generated in the exhaust gas, the plasma

excited species are produced by the collision between electrons released from electrodes and gas molecules. The plasma excited species include large numbers of $O(^1D)$ radicals, hydroxide excited species OH^* , per-hydroxide excited species HOO^* and the like each having a strong oxidizing force, and hence the carbon solid fraction is oxidized by the plasma excited species. The carbon solid fraction is liable to be electrically charged in the plasma, so that there is generated a phenomenon that the carbon solid fraction is oxidized efficiently in a state in which they have been collected electrostatically on the electrodes. The significance of the preliminary removal of the soluble organic fraction from the surface of the particulate material resides in this point. The conversion of the carbon solid fraction by the oxidization as described above is conducted continuously and moreover at a relatively low temperature.

A plasma generating device has a good gas permeability, as compared with a filter, so that even if the plasma generating device is incorporated in an exhaust pipe, an increase in exhausting resistance is suppressed to a low level. Therefore, an influence cannot be exerted to an engine output.

At least one selected from the group consisting of Pt, Pd, Rh, Cu, Ag and Au is used as the catalyst.

If an intensity E of electric field is set at a value equal to or larger than 3.0 kV/mm and a power density D_w is set at a value equal to or larger than 1 W/cm³ in the plasma generating conditions, the amount of released high-energy electrons existing in the plasma is increased, and hence the production of the plasma

excited species is efficiently conducted, whereby the conversion of the carbon solid fraction by the oxidization can be enhanced. However, if at least one of requirements of $E \geq 3.0$ kV/mm and $Dw \geq 1$ W/cm³ is lacked, the above-described effect cannot be obtained.

Further, if the surface of at least one of opposed electrodes which is opposed to the other electrodes is covered with a dielectric, the entire surface of the dielectric is uniformly charged upon application of a voltage. Therefore, the entire space between the dielectric and the other electrode opposed to the dielectric constitutes a plasma space, so that the frequency of random contact between the carbon solid fraction and the plasma excited species can be increased to enhance the conversion of the carbon solid fraction by the oxidization. If opposed surfaces of the opposed electrodes are covered with dielectrics, respectively, an increase in the applied voltage is brought about with an increase in impedance, but it is possible to provide a converting performance equivalent to that in the case where the one surface is covered, by setting the plasma generating conditions as described above.

Further, according to the present invention, there is provided a process for decreasing the content of a particulate material contained in an exhaust gas from a lean burn engine or the like, comprising the steps of: generating plasma in the exhaust gas discharged from the lean burn engine and containing the particulate material to produce a plurality of nitrogen dioxide molecules and a plurality of ozone molecules; and oxidizing the

particulate material by the nitrogen dioxide molecules and the ozone molecules.

When the plasma is generated in the exhaust gas, the following process is provided: oxygen atom excited species are produced by the collision between released electrons and oxygen molecules → ozone is produced by the reaction of the oxygen atom excited species with oxygen molecules → nitrogen dioxide (NO_2) is produced by the reaction of ozone with nitrogen monoxide (NO). The productions of the nitrogen dioxide and ozone are carried out independent of the temperature of the exhaust gas. The particulate material PM is oxidized and converted based on the reaction represented by $\text{PM} + \text{NO}_2 + \text{O}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2$. The conversion of the particulate material by the oxidization is conducted continuously and moreover at a relatively low temperature.

A plasma generating device has a good gas permeability, as compared with a filter, so that even if the plasma generating device is incorporated in an exhaust pipe, an increase in exhausting resistance is suppressed to a low level. Therefore, an influence cannot be exerted to an engine output.

Yet further, according to the present invention, there is provided a process for decreasing the content of a particulate material contained in an exhaust gas from a lean burn engine, comprising the steps of: generating plasma in the exhaust gas discharged from the lean burn engine and containing the particulate material to produce a plurality of nitrogen dioxide molecules and a plurality of ozone molecules; oxidizing the particulate material

by the nitrogen dioxide molecules and the ozone molecules; and subjecting the particulate material to the reaction with the nitrogen dioxide molecules and the ozone molecules in the presence of a catalyst to oxidize the particulate material.

If the catalyst is used as described above, the above-described reaction, namely, the reaction represented by $\text{PM} + \text{NO}_2 + \text{O}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2$ can be promoted to greatly increase the decrement rate of the particulate material.

At least one selected from the group consisting of Pt, Pd, Rh, Cu, Ag and Au is used as the catalyst.

If an intensity E of electric field is set at a value equal to or larger than 3.0 kV/mm and a power density D_w is set at a value equal to or larger than 1 W/cm³ in the plasma generating conditions, the amount of released high-energy electrons existing in the plasma is increased, and hence the productions of the nitrogen dioxide and ozone are efficiently conducted, whereby the conversion of the carbon solid fraction by the oxidization can be enhanced. However, if at least one of requirements of $E \geq 3.0$ kV/mm and $D_w \geq 1$ W/cm³ is lacked, the above-described effect cannot be obtained.

Further, if the surface of at least one of opposed electrodes which is opposed to the other electrodes is covered with a dielectric, the entire surface of the dielectric is uniformly charged upon application of a voltage. Therefore, the entire space between the dielectric and the other electrode opposed to the dielectric constitutes a plasma space, so that the frequency

of random contact of the particulate material with the nitrogen dioxide and ozone can be increased to enhance the conversion of the carbon solid fraction by the oxidization. If opposed surfaces of the opposed electrodes are covered with dielectrics, respectively, an increase in the applied voltage is provided by an increase in impedance, but it is possible to provide a converting performance equivalent to that in the case where the one surface is covered, by setting the plasma generating conditions as described above.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is an illustration of a first embodiment of an equipment for a particulate material content decreasing test.

Fig.2 is a diagram of a plasma generating device.

Fig.3 is a graph showing amounts of a particulate material before and after a plasma treatment.

Fig.4 is an illustration of a second embodiment of an equipment for a particulate material content decreasing test.

Fig.5 is a graph showing amounts of a particulate material before and after a catalytic reaction and after a plasma treatment for Example 4.

Fig.6 is a graph showing amounts of a particulate material before and after a catalytic reaction and after a plasma treatment for Example 5.

Fig.7 is an illustration of a third embodiment of an equipment for a particulate material content decreasing test.

Fig.8 is a graph showing amounts of a particulate material

before and after a plasma treatment and after a catalytic reaction for Example 6.

Fig.9 is a graph showing amounts of a particulate material before and after a plasma treatment and after a catalytic reaction for Example 7.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(Embodiment I)

In an equipment 1 for a particulate material content-decreasing test shown in Fig.1, a commercially available diesel generator 2 is selected as a source of generating an exhaust gas containing a particulate material. A first flow rate regulating valve 4_1 is mounted in an exhaust pipe 3 of the diesel generator 2. In the exhaust pipe 3, a conduit 5 is connected at one end between the diesel generator 2 and the first flow rate regulating valve 4_1 . A second flow rate regulating valve 4_2 , a heater 6, a plasma generating device PG and a flow-meter 8 are mounted in the exhaust pipe 3 sequentially in the named order from the side of the exhaust pipe 3. The other end of the conduit 5 opens to the atmosphere.

In the conduit 5, a first branch pipe 9_1 is connected at one end between the heater 6 and the plasma generating device PG, and at the other end to a first port p_1 of a three-way valve 10. In the conduit 5, a second branch pipe 9_2 is also connected at one end between the plasma generating device PG and the flow-meter 8, and at the other end to a second port p_2 of the three-way valve 10. Another conduit 11 is connected at one end to a third port

p_3 of the three-way valve 10, and at the other end to a suction port of a suction pump 12. A filter 13 is mounted in the conduit 11.

The diesel generator 2 is EXT12D made by Honda Motor Co., Ltd., and the specification thereof is as follows: the type of an engine: a water-cooled 3-cylinder and 4-cycle diesel engine; a total displacement: 1061 cc; a fuel used: diesel light oil; a rated output: 12 kVA. The filter 13 is a Teflon-coated filter made by German Laboratory, and has a mesh size of 0.3 μm mesh.

Referring to Fig.2, the plasma generating device PG includes a plurality of first to sixth electrodes 14₁ to 14₆ made of a metal, each of which is formed into a plate shape in the illustrated embodiment. The first to sixth electrodes 14₁ to 14₆ are mounted in a housing 15 (see Fig.1) so that they are parallel to a direction A of flowing of an exhaust gas, and the adjacent electrodes 14₁ and 14₂; 14₂ and 14₃; 14₃ and 14₄; 14₄ and 14₅; 14₅ and 14₆ are opposed to each other. The surface of the first electrode 14₁ located at one end, which is opposed to the second electrode 14₂, is a non-coated metal surface, but the surface of the second electrode 14₂, which is opposed to the first electrode 14₁, is coated entirely with a dielectric 16. The arrangement relationship between the opposed surfaces of the first and second electrodes 14₁ and 14₂ applies to those between the second and third electrodes 14₂ and 14₃; between the third and fourth electrodes 14₃ and 14₄; between the fourth and fifth electrodes 14₄ and 14₅; and between the fifth and sixth electrodes 14₅ and 14₆. The first, third and fifth

electrodes 14₁, 14₃ and 14₅ are connected to a power source 18 through lead wires 17, while the second, fourth and sixth electrodes 14₂, 14₄ and 14₆ are earthed through lead wires 19.

If the plasma generating device PG is constructed as described above, the entire surface of each of the dielectrics 16 is uniformly charged upon application of a voltage, and hence the entire space between each of the dielectrics 16 and each of the electrodes 14₁ to 14₆ which is opposed thereto constitutes a plasma space Pp. Namely, the plasma spaces Pp are formed between the first and second electrodes 14₁ and 14₂; between the second and third electrodes 14₂ and 14₃; between the third and fourth electrodes 14₃ and 14₄; between the fourth and fifth electrodes 14₄ and 14₅; and between the fifth and sixth electrodes 14₅ and 14₆. That is, each of the plasma spaces Pp is defined by the opposed electrodes.

Each of the first to sixth electrodes 14₁ to 14₆ is formed of a stainless steel (e.g., JIS SUS316), and has a size of 20 mm long, 50 mm wide and 1.0 mm thick, with a transverse side extending along the exhaust gas flowing direction A. Each of the dielectrics 16 comprises an alumina (Al₂O₃) layer having a thickness of 0.5 mm, which is bonded to each of the second to sixth electrodes 14₂ to 14₆ by the mechanical pressing. The adhesion using an adhesive, the flame spraying or the like may be also utilized for such bonding. A gap g in each of the plasma spaces Pp, namely, a distance between each of the adjacent electrodes 14₁ to 14₆ and each of the dielectrics 16 is 0.5 mm.

A particulate material content reducing test was carried

out using the above-described equipment 1, according to the following procedure:

(1) The diesel generator 2 was operated, and an exhaust gas discharged from the diesel generator 2 was caused to flow through the exhaust gas 3 and the conduit 5.

(2) The flow rate of the testing exhaust gas flowing through the conduit 5, and hence through the plasma generating device PG, was regulated to 7.0 L/min by the first and second flow rate regulating valves 4_1 and 4_2 , while being measured by the flow-meter 8.

(3) The heater 6 was operated to heat the exhaust gas having a temperature of about 70°C up to 150°C, and the exhaust gas was allowed to flow through the first and third ports p_1 and p_3 of the three-way valve 10. Then, the testing exhaust gas flowing through the conduit 5 was diverted into the first branch pipe 9_1 by driving the suction pump 12 at a suction rate of 5.0 L/min, and caused to flow through the filter 13 over 10 minutes, whereby a particulate material in the testing exhaust gas was collected by the filter 13. A weight of the particulate material collected was determined from the weights of the filter before and after the collection of the particulate material, and defined as an amount of the particulate material before a plasma treatment.

(4) The plasma generating device PG was operated, and the second and third ports P_2 and P_3 were put into communication with each other by switching-over of the three-way valve 10. Then, the testing exhaust gas discharged from the plasma generating device PG and flowing through the conduit 5, was diverted into the second,

branch pipe 9₂ by driving the suction pump 12 at a suction rate of 5.0 L/min, and caused to flow through a new filter 13 over 10 minutes, whereby the particulate material in the testing exhaust gas was collected by the new filter 13. A weight of the particulate material collected was determined from the weights of the filter before and after the collection of the particulate material, and defined as an amount of the particulate material after the plasma treatment.

In the test, an excitation spectrum of the exhaust gas was analyzed as a plasma excited state of the exhaust gas within the plasma generating device PG by an emission spectrometric photometer (IMUC-7000 made by Otsuka Electronics Co., Ltd.). As a result, the production of a plurality of excited-oxygen atoms by the generation of plasma was observed. Particularly, because an excitation spectrum of 6eV or more was present, the existence of O(¹D) radicals was considered to be present. Thus, it can be said that a plurality of hydroxide excited species and per-hydroxide excited species HOO* were produced.

Table 1 shows plasma generating conditions for Examples 1 to 3.

Table 1

| Example | Plasma space | | Electricity input conditions | | | | Intensity E of electric field (kV/mm) | Power density Dw (W/cm ³) |
|---------|--------------|---------------------------|------------------------------|----------------|-----------------|-----------|---------------------------------------|---------------------------------------|
| | Gap (mm) | Volume (cm ³) | Alternate current | Frequency (Hz) | Voltage (kVp-p) | Power (W) | | |
| 1 | 0.5 | 2.5 | Sine wave AC | 300 | 3.0 | 2.7 | 3.0 | 1.1 |
| 2 | 1.5 | 7.5 | Sine wave AC | 700 | 8.2 | 9.1 | 2.7 | 1.2 |
| 3 | 0.5 | 2.5 | Sine wave AC | 100 | 3.0 | 2.1 | 3.0 | 0.8 |

In Table 1, the intensity E of electric field is a value provided by dividing a voltage $[(kV_{p-p})/2]$ applied between the opposed electrodes such as between the first and second electrodes 14_1 and 14_2 by the gap g (mm), and the power density Dw is a value provided by dividing a power $(0.54 \text{ W} \times 5 = 2.7 \text{ W})$ in the plasma space P_p defined by the opposed electrodes by a volume $[(2 \text{ cm} \times 5 \text{ cm} \times 0.05 \text{ cm}) \times 5 = 2.5 \text{ cm}^3]$ of the plasma space P_p .

Table 2 shows amounts of the particulate material before and after the plasma treatment, and decrement amounts and decrement rates of the particulate material decreased by the plasma treatment for Examples 1 to 3.

Table 2

| | Particulate material | | | |
|-----------|---|--|--------------------------|-----------------------|
| | Amount (mg) before plasma treatment | Amount (mg) after plasma treatment | Decrement amount (mg) | Decrement rate (%) |
| Example 1 | 1.3 | 0.2 | 1.1 | 84.6 |
| Example 2 | 1.2 | 0.7 | 0.5 | 41.7 |
| Example 3 | 1.4 | 0.8 | 0.6 | 42.9 |

Fig.3 is a graph based on Table 2 and showing amounts of the particulate material before and after the plasma treatment for Examples 1 to 3. As apparent from Tables 1 and 2 and Fig.3,

according to Example 1, per-hydroxide excited species HOO^* can be efficiently produced by setting the intensity E of electric field at a value equal to or larger than 3.0 kV/mm and the power density D_w at a value equal to or larger than 1 W/cm^3 , whereby the decrement rate of the particulate material can be increased to about 84.6% . The intensity E of electric field is preferably in a range of $3 \text{ kV/mm} \leq E \leq 15 \text{ kV/mm}$, and the power density D_w is preferably in a range of $1 \text{ W/cm}^3 \leq D_w \leq 10 \text{ W/cm}^3$.

In the cases of Examples 2 and 3, the decrement rate of the particulate material is lower and approximately half of that in Example 1, because one of the intensity E of electric field and the power density D_w does not satisfy the above-described requirement.

Embodiment I is applicable for decreasing the content of a particulate material contained in an exhaust gas discharged from an automobile, a factory or the like.

According to the above-described process, it is possible to continuously convert the particulate material contained in the exhaust gas from the lean burn engine or the like by the oxidization, to thereby remarkably decrease the content thereof. In addition, this process cannot provide a disadvantage that the exhausting resistance is greatly increased to affect an engine output.

(Embodiment II)

In an equipment 1 for a particulate material content

decreasing test shown in Fig.4, a commercially available diesel generator 2 is selected as a source of generating an exhaust gas containing a particulate material. A first flow rate regulating valve 4_1 is mounted in an exhaust pipe 3 of the diesel generator 2. In the exhaust pipe 3, a conduit 5 is connected at one end between the diesel generator 2 and the first flow rate regulating valve 4_1 , and a second flow rate regulating valve 4_2 , a heater 6, a catalytic reactor CR, a plasma generating device PG and a flow-meter 8 are mounted on the exhaust pipe 3 sequentially in the named order from the side of the exhaust pipe 3. The other end of the conduit 5 opens to the atmosphere.

In the conduit 5, a first branch pipe 9_1 is connected at one end between the heater 6 and the catalytic reactor CR, and at the other end to a suction port of a suction pump 12. A first on-off valve 20_1 and a filter 13 are mounted in the first branch pipe 9_1 sequentially from the side of the conduit 5. In the conduit 5, a second branch pipe 9_2 is also connected at one end between the catalytic reactor CR and the plasma generating device PG, and at the other end between the first on-off valve 20_1 and the filter 13 in the first branch pipe 9_1 . A second on-off valve 20_2 is mounted in the second branch pipe 9_2 . Further, in the conduit 5, a third branch pipe 9_3 is connected at one end between the plasma generating device PG and the flow-meter 8, and at the other end between a connection of the second branch pipe 9_2 and the filter 13 in the first branch pipe 9_1 . A third

on-off valve 20₃ is mounted in the third branch pipe 9₃.

As in Embodiment I, the diesel generator 2 is EXT12D made by Honda Motor Co. Ltd., and the specification thereof is as follows: the type of an engine: a water-cooled 3-cylinder and 4-cycle diesel engine; a total displacement: 1061 cc; a fuel used: diesel light oil; a rated output: 12 kVA. The filter 13 is a Teflon-coated filter made by German Laboratory, and has a mesh size of 0.3 μ m mesh.

As shown in Fig.2, the plasma generating device PG has the same structure as that in Embodiment I and includes a plurality of first to sixth electrodes 14₁ to 14₆ made of a metal, each of which is formed into a plate shape in the illustrated embodiment. The first to sixth electrodes 14₁ to 14₆ are mounted in a housing 15 (see Fig.4) so that they are parallel to a direction A of flowing of an exhaust gas, and the adjacent electrodes 14₁ and 14₂; 14₂ and 14₃; 14₃ and 14₄; 14₄ and 14₅; 14₅ and 14₆ are opposed to each other. The surface of the first electrode 14₁ located at one end, which is opposed to the second electrode 14₂, is a non-coated metal surface, but the surface of the second electrode 14₂, which is opposed to the first electrode 14₁, is coated entirely with a dielectric 16. The arrangement relationship between the opposed surfaces of the first and second electrodes 14₁ and 14₂ applies to those between the second and third electrodes 14₂ and 14₃; between the third and fourth electrodes 14₃ and 14₄; between the fourth and fifth

electrodes 14₄ and 14₅; and between the fifth and sixth electrodes 14₅ and 14₆. The first, third and fifth electrodes 14₁, 14₃ and 14₅ are connected to a power source 18 through lead wires 17, while the second, fourth and sixth electrodes 14₂, 14₄ and 14₆ are earthed through lead wires 19.

If the plasma generating device PG is constructed as described above, the entire surface of each of the dielectrics 16 is uniformly charged upon application of a voltage, and hence the entire space between each of the dielectrics 16 and each of the electrodes 14₁ to 14₆ which is opposed thereto constitutes a plasma space Pp. Namely, the plasma spaces Pp are formed between the first and second electrodes 14₁ and 14₂; between the second and third electrodes 14₂ and 14₃; between the third and fourth electrodes 14₃ and 14₄; between the fourth and fifth electrodes 14₄ and 14₅; and between the fifth and sixth electrodes 14₅ and 14₆. That is, each of the plasma spaces Pp is defined by the opposed electrodes.

Each of the first to sixth electrodes 14₁ to 14₆ is formed of a stainless steel (e.g., JIS SUS316), and has a size of 20 mm long, 50 mm wide and 1.0 mm thick, with a transverse side extending along the exhaust gas flowing direction A. Each of the dielectrics 16 comprises an alumina (Al₂O₃) layer having a thickness of 0.5 mm, which is bonded to each of the second to sixth electrodes 14₂ to 14₆ by the mechanical pressing. The adhesion using an adhesive, the flame spraying or the like may

be also utilized for such bonding. A gap g in each of the plasma spaces P_p , namely, a distance between each of the adjacent electrodes 14_1 to 14_6 and each of the dielectric 16 is 0.5 mm.

The catalytic reactor CR comprises a honeycomb carrier and platinum (Pt) carried as a catalyst on the honeycomb carrier, and is placed in a housing 21. To carry platinum on the honeycomb carrier, the following process was adopted: (i) 80 grams of a solution of platinum dinitrodiamine nitric acid $[Pt(NH_3)_2(NO_2)_2 \cdot HNO_3]$ containing 5 % by weight of platinum, 96 grams of commercially available $\gamma-Al_2O_3$, and 1,000 grams of ion-exchange water were mixed together, and at the same time, an excessive amount of water was removed; (ii) a mixture was dried at $200^\circ C$ for 2 hours; (iii) a powder of Al_2O_3 carrying platinum was produced by calcining the mixture at $600^\circ C$ for 2 hours; (iv) 90 grams of the powder of Al_2O_3 carrying platinum, 50 grams of an SiO_2 binder (containing 20 % by weight of SiO_2) and 150 grams of ion-exchange water were mixed together; (v) a slurry was prepared by wet-pulverizing the mixture over 12 hours using alumina balls; (vi) a honeycomb carrier carrying a platinum catalyst in an amount of 4g/L at a wash coat amount of 100 g/L was prepared by repeating a process: immersing a honeycomb carrier made of cordierite and having a volume of about 30 L (a diameter of 2.54 and a length of 60 mm) with 400 cells/in² and 6 mils into the slurry; removing an excessive amount of the slurry from the carrier by jet water injection

after the removal of the carrier; and drying the carrier at 150°C for 1 hour; (vii) the honeycomb carrier was calcined at 500°C for 2 hours; (viii) the honeycomb carrier carrying the catalyst was placed into the housing 21.

This type of catalytic reactor CR has a structure substantially same as that of a catalytic converter, and hence the exhausting resistance cannot be greatly increased.

A particulate material content-decreasing test was carried out using the above-described equipment by the following procedure:

(1) The diesel generator 2 was operated, and an exhaust gas discharged from the diesel generator 2 was caused to flow through the exhaust gas 3 and the conduit 5.

(2) The flow rate of the testing exhaust gas flowing through the conduit 5, and hence through the catalytic reactor CR and the plasma generating device PG, was regulated to 7.0 L/min by the first and second flow rate regulating valves 4_1 and 4_2 , while being measured by the flow-meter 8.

(3) The heater 6 was operated to heat the exhaust gas having a temperature of about 70°C up to 150°C, and the first on-off valve 20_1 was opened, while the second and third on-off valves 20_2 and 20_3 were closed. Then, the testing exhaust gas flowing through the conduit 5 was diverted into the first branch pipe 9_1 by driving the suction pump 12 at a suction rate of 5.0 L/min, and caused to flow through the filter 13 over 20 minutes, whereby

a particulate material in the testing exhaust gas was collected by the filter 13. A weight of the particulate material collected was determined from the weights of the filter before and after the collection of the particulate material, and was defined as an amount of the particulate material before a catalytic reaction.

(4) The second on-off valve 20_2 was opened, while the first and third on-off valves 20_1 and 20_3 were closed. Then, the testing exhaust gas flowing through the conduit 5 via the catalytic reactor CR, was diverted into the second branch pipe 9_2 by driving the suction pump 12 at a suction rate of 5.0 L/min, and caused to flow through a new filter 13 over 20 minutes, whereby the particulate material in the testing exhaust gas was collected by the new filter 13. A weight of the particulate material collected was determined from the weights of the filter before and after the collection of the particulate material, and defined as an amount of the particulate material after the catalytic reaction.

(5) The plasma generating device PG was operated, and the third on-off valve 20_3 was opened, while the first and second on-off valves 20_1 and 20_2 were closed. Then, the testing exhaust gas flowing through the conduit 5 via the catalytic reactor CR and the plasma generating device PG, was diverted into the third branch pipe 9_3 by driving the suction pump 12 at a suction rate of 5.0 L/min, and caused to flow through a new filter 13 over

20 minutes, whereby the particulate material in the testing exhaust gas was collected by the new filter 13. A weight of the particulate material collected was determined from the weights of the filter before and after the collection of the particulate material, and defined as an amount of the particulate material after the plasma treatment.

The process using platinum as the catalyst as described above is defined as Example 4.

A particulate material content-decreasing test was carried out as Example 5 in a similar manner, except that a catalytic reactor CR having silver (Ag) as a catalyst was used, and the temperature of an exhaust gas flowing into the plasma generating device PG was set at 250°C. To carry silver (Ag) on Al_2O_3 in a catalyst-carried honeycomb carrier, this process was the same as Example 3, except that a mixture comprising 4.72 grams of silver nitrate (AgNO_3), 97 grams of commercially available $\gamma\text{-Al}_2\text{O}_3$, and 1,000 grams of ion-exchange water were used as a silver-containing solution, and the amount of silver carried on the honeycomb carrier was set at 3 g/L.

In each of Examples 4 and 5, an excitation spectrum of the exhaust gas was analyzed as a plasma excited state of the exhaust gas within the plasma generating device PG by an emission spectrometric photometer (IMUC-7000 made by Otsuka Electronics Co., Ltd.). As a result, the production of a plurality of excited-oxygen atoms by the generation of plasma

was observed. Particularly, because an excitation spectrum of 6eV or more was present, $O(^1D)$ radicals was considered to be present. Thus, it can be said that if the plasma is generated in the exhaust gas, $O(^1D)$ radicals and ozone excited species are produced by the collision between electrons released from the electrodes and oxygen atoms \rightarrow hydroxide excited species OH^* are produced by the reaction of $O(^1D)$ radicals and ozone excited species with water \rightarrow per-hydroxide excited species HOO^* having a strong oxidizing force are produced by the reaction of the hydroxide excited species OH^* with oxygen. Namely, the plasma excited species include $O(^1D)$ radicals, hydroxide excited species OH^* , per-hydroxide excited species HOO^* and the like.

Table 3 shows plasma generating conditions for Examples 4 and 5.

Table 3

| Example | Plasma space | | Electricity input conditions | | | | Intensity E of electric field (kV/mm) | Power density Dw (W/cm ³) |
|---------|--------------|---------------------------|------------------------------|----------------|-----------------|-----------|---------------------------------------|---------------------------------------|
| | Gap (mm) | Volume (cm ³) | Alternate current | Frequency (Hz) | Voltage (kVp-p) | Power (W) | | |
| 4 | 0.5 | 2.5 | Sine wave AC | 2,500 | 7.6 | 7.4 | 7.6 | 3.0 |
| 5 | 0.5 | 2.5 | Sine wave AC | 1,600 | 7.2 | 9.5 | 7.2 | 3.8 |

In Table 3, the intensity E of electric field is a value provided by dividing a voltage $[(kV_{p-p})/2]$ applied between the opposed electrodes such as between the first and second electrodes 14_1 and 14_2 by the gap g (mm), and the power density Dw is a value provided by dividing a power (Example 4: $1.48 \text{ W} \times 5 = 7.4 \text{ W}$; and Example 5: $1.9 \text{ W} \times 5 = 9.5 \text{ W}$) in the plasma space Pp defined by the opposed electrodes by a volume $[(2 \text{ cm} \times 5 \text{ cm} \times 0.05 \text{ cm}) \times 5 = 2.5 \text{ cm}^3]$ of the plasma space Pp .

Table 4 shows amounts of the particulate material before and after the catalytic reaction and after the plasma treatment, and decrement amounts and decrement rates of the particulate material decreased by the catalytic reaction and the plasma treatment for Examples 4 and 5.

Table 4

| Example | Particulate material | | | | | | |
|---------|---------------------------------------|--------------------------|-----------------------|--------------------|------------------------|-----------------------|--------------------|
| | Amount before catalytic reaction (mg) | After catalytic reaction | | | After plasma treatment | | |
| | | Amount (mg) | Decrement amount (mg) | Decrement rate (%) | Amount (mg) | Decrement amount (mg) | Decrement rate (%) |
| 4 | 2.6 | 1.9 | 0.7 | 26.9 | 0.2 | 2.4 | 92.3 |
| 5 | 2.4 | 1.7 | 0.7 | 29.2 | 0.2 | 2.2 | 91.7 |

Figs.5 and 6 are graphs based on Table 4 and showing amounts of the particulate material before and after the catalytic reaction and after the plasma treatment for Examples 4 and 5. As apparent from Tables 3 and 4 and Figs.5 and 6, according to Examples 4 and 5, plasma excited species can be efficiently produced by setting the intensity E of electric field at a value equal to or larger than 3.0 kV/mm and setting the power density D_w at a value equal to or larger than 1 W/cm^3 , whereby the decrement rate of the particulate material can be increased up to about 92 % or more. The intensity E of electric field is preferably in a range of $3 \text{ kV/mm} \leq E \leq 15 \text{ kV/mm}$, and the power density D_w is preferably in a range of $1 \text{ W/cm}^3 \leq D_w \leq 10 \text{ W/cm}^3$.

The particulate material before the catalytic reaction was subjected to an extraction using a Soxhlet extractor. As a result, an amount of a fraction soluble in an organic solvent was about 30 % by weight, and an amount of carbon solid fraction was about 70 % by weight. If Table 4 is reviewed with this fact in mind, it can be seen that substantially all the fraction soluble in the organic solvent was converted for purification of the exhaust gas by the catalytic reaction, and the conversion of the carbon solid fraction for purification of the exhaust gas was efficiently carried out by the subsequent plasma treatment.

Embodiment II is applicable for decreasing the content of a particulate material contained in an exhaust gas discharged from an automobile, a factory or the like.

According to the above-described process, it is possible to continuously convert a particulate material contained in an exhaust gas from a lean burn engine or the like by the oxidization, to thereby remarkably decrease the content of the particulate material. In addition, this process cannot provide a disadvantage that the exhausting resistance is greatly increased to affect an engine output.

(Embodiment III)

In an equipment 1 for a particulate material content-decreasing test shown in Fig.7, a commercially available diesel generator 2 is selected as a source of generating an exhaust gas containing a particulate material. A first flow rate regulating valve 4_1 is mounted in an exhaust pipe 3 of the diesel generator 2. In the exhaust pipe 3, a conduit 5 is connected at one end between the diesel generator 2 and the first flow rate regulating valve 4_1 , and a second flow rate regulating valve 4_2 , a heater 6, a plasma generating device PG, a catalytic reactor CR and a flow-meter 8 are mounted on the exhaust pipe 3 sequentially in the named order from the side of the exhaust pipe 3. The other end of the conduit 5 opens to the atmosphere.

In the conduit 5, a first branch pipe 9_1 is connected at one end between the heater 6 and the plasma generating device

PG, and at the other end to a suction port of a suction pump 12. A first on-off valve 20_1 and a filter 13 are mounted in the first branch pipe 9_1 sequentially from the side of the conduit 5. In the conduit 5, a second branch pipe 9_2 is also connected at one end between the plasma generating device PG and the catalytic reactor CR, and at the other end between the first on-off valve 20_1 and the filter 13 in the first branch pipe 9_1 . A second on-off valve 20_2 is mounted in the second branch pipe 9_2 . Further, in the conduit 5, a third branch pipe 9_3 is connected at one end between the catalytic reactor CR and the flow-meter 8, and at the other end between a connection of the second branch pipe 9_2 and the filter 13 in the first branch pipe 9_1 . A third on-off valve 20_3 is mounted in the third branch pipe 9_3 .

As in Embodiments I and II, the diesel generator 2 is EXT12D made by Honda Motor Co. Ltd., and the specification thereof is as follows: the type of an engine: a water-cooled 3-cylinder and 4-cycle diesel engine; a total displacement: 1061 cc; a fuel used: diesel light oil; a rated output: 12 kVA. The filter 13 is a Teflon-coated filter made by German Laboratory, and has a mesh size of 0.3 μm mesh.

As shown in Fig.2, the plasma generating device PG has the same structure as that in Embodiments I and II, and includes a plurality of first to sixth electrodes 14_1 to 14_6 made of a metal, each of which is formed into a plate shape in the

illustrated embodiment. The first to sixth electrodes 14_1 to 14_6 are mounted in a housing 15 (see Fig.7) so that they are parallel to a direction A of flowing of an exhaust gas, and the adjacent electrodes 14_1 and 14_2 ; 14_2 and 14_3 ; 14_3 and 14_4 ; 14_4 and 14_5 ; 14_5 and 14_6 are opposed to each other. The surface of the first electrode 14_1 located at one end, which is opposed to the second electrode 14_2 , is a non-coated metal surface, but the surface of the second electrode 14_2 , which is opposed to the first electrode 14_1 , is coated entirely with a dielectric 16. The arrangement relationship between the opposed surfaces of the first and second electrodes 14_1 and 14_2 applies to those between the second and third electrodes 14_2 and 14_3 ; between the third and fourth electrodes 14_3 and 14_4 ; between the fourth and fifth electrodes 14_4 and 14_5 ; and between the fifth and sixth electrodes 14_5 and 14_6 . The first, third and fifth electrodes 14_1 , 14_3 and 14_5 are connected to a power source 18 through lead wires 17, while the second, fourth and sixth electrodes 14_2 , 14_4 and 14_6 are earthed through lead wires 19.

If the plasma generating device PG is constructed as described above, the entire surface of each of the dielectrics 16 is uniformly charged upon application of a voltage, and hence the entire space between each of the dielectrics 16 and each of the electrodes 14_1 to 14_6 which is opposed thereto constitutes a plasma space Pp. Namely, the plasma spaces Pp are formed between the first and second electrodes 14_1 and 14_2 ; between

the second and third electrodes 14_2 and 14_3 ; between the third and fourth electrodes 14_3 and 14_4 ; between the fourth and fifth electrodes 14_4 and 14_5 ; and between the fifth and sixth electrodes 14_5 and 14_6 . That is, each of the plasma spaces P_p is defined by the opposed electrodes.

Each of the first to sixth electrodes 14_1 to 14_6 is formed of a stainless steel (e.g., JIS SUS316), and has a size of 20 mm long, 50 mm wide and 1.0 mm thick, with a transverse side extending along the exhaust gas flowing direction A. Each of the dielectrics 16 comprises an alumina (Al_2O_3) layer having a thickness of 0.5 mm, which is bonded to each of the second to sixth electrodes 14_2 to 14_6 by the mechanical pressing. The adhesion using an adhesive, the flame spraying or the like may be also utilized for such bonding. A gap g in each of the plasma spaces P_p , namely, a distance between each of the adjacent electrodes 14_1 to 14_6 and each of the dielectric 16 is 0.5 mm.

The catalytic reactor CR comprises a honeycomb carrier and platinum (Pt) carried as a catalyst on the honeycomb carrier, and is placed in a housing 21. To carry platinum on the honeycomb carrier, the following process was adopted: (i) 80 grams of a solution of platinum dinitrodiamine nitric acid $[Pt(NH_3)_2(NO_2)_2 \cdot HNO_3]$ containing 5 % by weight of platinum, 96 grams of commercially available $\gamma-Al_2O_3$, and 1,000 grams of ion-exchange water were mixed together, and at the same time, an excessive amount of water was removed; (ii) a mixture was

dried at 200°C for 2 hours; (iii) a powder of Al_2O_3 carrying platinum was produced by calcining the mixture at 600°C for 2 hours; (iv) 90 grams of the powder of Al_2O_3 having platinum carried thereon, 50 grams of an SiO_2 binder (containing 20 % by weight of SiO_2) and 150 grams of ion-exchange water were mixed together; (v) a slurry was prepared by wet-pulverizing the mixture over 12 hours using alumina balls; (vi) a honeycomb carrier carrying a platinum catalyst in an amount of 4g/L at a wash coat amount of 100 g/L was prepared by repeating a process: immersing a honeycomb carrier made of cordierite and having a volume of about 30 L (a diameter of 2.54 and a length of 60 mm) with 400 cells/in² and 6 mils into the slurry; removing an excessive amount of the slurry from the carrier by jet water injection after the removal of the carrier; and drying the carrier at 150°C for 1 hour; (vii) the honeycomb carrier was calcined at 500°C for 2 hours; (viii) the honeycomb carrier carrying the catalyst was placed into the housing 21.

This type of catalytic reactor CR has a structure substantially same as that of a catalytic converter, and hence the exhausting resistance cannot be greatly increased.

A particulate material content-decreasing test was carried out using the above-described equipment by the following procedure:

(1) The diesel generator 2 was operated, and an exhaust gas discharged from the diesel generator 2 was caused to flow

through the exhaust gas 3 and the conduit 5.

(2) The flow rate of the testing exhaust gas flowing through the conduit 5, and hence through the plasma generating device PG and the catalytic reactor CR, was regulated to 7.0 L/min by the first and second flow rate regulating valves 4_1 and 4_2 , while being measured by the flow-meter 8.

(3) The heater 6 was operated to heat the exhaust gas having a temperature of about 70°C up to 150°C, and the first on-off valve 20_1 was opened, while the second and third on-off valves 20_2 and 20_3 were closed. Then, the testing exhaust gas flowing through the conduit 5 was diverted into the first branch pipe 9_1 by driving the suction pump 12 at a suction rate of 5.0 L/min, and caused to flow through the filter 13 over 20 minutes, whereby a particulate material in the testing exhaust gas was collected by the filter 13. A weight of the particulate material collected was determined from the weights of the filter before and after the collection of the particulate material, and was defined as an amount of the particulate material before a catalytic reaction.

(4) The plasma generating device PG was operated, and the second on-off valve 20_2 was opened, while the first and third on-off valves 20_1 and 20_3 were closed. Then, the testing exhaust gas discharged from the plasma generating device PG and flowing through the conduit 5 via the catalytic reactor CR, was diverted into the second branch pipe 9_2 by driving the suction pump 12

at a suction rate of 5.0 L/min, and caused to flow through a new filter 13 over 20 minutes, whereby the particulate material in the testing exhaust gas was collected by the new filter 13. A weight of the particulate material collected was determined from the weights of the filter before and after the collection of the particulate material, and defined as an amount of the particulate material after the plasma treatment.

(5) In a state in which the plasma generating device PG was operated, the third on-off valve 20_3 was opened, while the first and second on-off valves 20_1 and 20_2 were closed. Then, the testing exhaust gas flowing through the conduit 5 via the plasma generating device PG and the catalytic reactor CR, was diverted into the third branch pipe 93 by driving the suction pump 12 at a suction rate of 5.0 L/min, and caused to flow through a new filter 13 over 20 minutes, whereby the particulate material in the testing exhaust gas was collected by the new filter 13. A weight of the particulate material collected was determined from the weights of the filter before and after the collection of the particulate material, and defined as an amount of the particulate material after the catalytic reaction.

The process using platinum as the catalyst as described above is defined as Example 6.

A particulate material content-decreasing test was carried out as Example 7 in a similar manner, except that a catalytic reactor CR having silver (Ag) as a catalyst was used,

and the temperature of an exhaust gas flowing into the plasma generating device PG was set at 250°C. To carry silver (Ag) on Al_2O_3 in a catalyst-carried honeycomb carrier, this process was the same as Example 6, except that a mixture comprising 4.72 grams of silver nitrate (AgNO_3), 97 grams of commercially available $\gamma\text{-Al}_2\text{O}_3$, and 1,000 grams of ion-exchange water were used as a silver-containing solution, and the amount of silver carried on the honeycomb carrier was set at 3 g/L.

In each of Examples 6 and 7, the exhaust gas upstream and the exhaust gas downstream of the plasma generating device PG was sampled, and the type of the gas was analyzed by FT-IR (a Fourier transform infrared spectroscopic device). As a result, the production of a plurality of nitrogen dioxide molecules and a plurality of ozone molecules by the generation of plasma was observed.

Table 5 shows plasma generating conditions for Examples 6 and 7.

Table 5

| Example | Plasma space | | Electricity input conditions | | | | Intensity E of electric field (kV/mm) | Power density Dw (W/cm ³) |
|---------|--------------|---------------------------|------------------------------|----------------|-----------------|-----------|---------------------------------------|---------------------------------------|
| | Gap (mm) | Volume (cm ³) | Alternate current | Frequency (Hz) | Voltage (kVp-p) | Power (W) | | |
| 6 | 0.5 | 2.5 | Sine wave AC | 200 | 7.6 | 3.1 | 7.6 | 1.2 |
| 7 | 0.5 | 2.5 | Sine wave AC | 500 | 6.6 | 8.5 | 6.6 | 3.4 |

In Table 5, the intensity E of electric field is a value provided by dividing a voltage $[(kV_{p-p})/2]$ applied between the opposed electrodes such as between the first and second electrodes 14_1 and 14_2 by the gap g (mm), and the power density Dw is a value provided by dividing a power (Example 6: $0.62 \text{ W} \times 5 = 3.1 \text{ W}$; and Example 7: $1.7 \text{ W} \times 5 = 8.5 \text{ W}$) in the plasma space Pp defined by the opposed electrodes by a volume $[(2 \text{ cm} \times 5 \text{ cm} \times 0.05 \text{ cm}) \times 5 = 2.5 \text{ cm}^3]$ of the plasma space Pp .

Table 6 shows amounts of the particulate material before and after the plasma treatment and after the catalytic reaction, and decrement amounts and decrement rates of the particulate material decreased by the plasma treatment and the catalytic reaction for Examples 6 and 7.

Table 6

| Example | Particulate material | | | | | | |
|---------|-------------------------------------|------------------------|-----------------------|--------------------------|-------------|-----------------------|--------------------|
| | Amount before plasma treatment (mg) | After plasma treatment | | After catalytic reaction | | | |
| | | Amount (mg) | Decrement amount (mg) | Decrement rate (%) | Amount (mg) | Decrement amount (mg) | Decrement rate (%) |
| 6 | 2.5 | 0.4 | 2.1 | 84.0 | 0.1 | 2.4 | 96.0 |
| 7 | 2.3 | 0.3 | 2.0 | 87.0 | 0.1 | 2.2 | 95.7 |

Figs.8 and 9 are graphs based on Table 6 and showing amounts of the particulate material before and after the plasma treatment and after the catalytic reaction for Examples 6 and 7. As apparent from Tables 5 and 6 and Figs.8 and 9, according to Examples 6 and 7, nitrogen dioxide and ozone can be efficiently produced by setting the intensity E of electric field at a value equal to or larger than 3.0 kV/mm and setting the power density D_w at a value equal to or larger than 1 W/cm^3 , whereby the decrement rate of the particulate material can be increased up to about 84 % or more. The intensity E of electric field is preferably in a range of $3 \text{ kV/mm} \leq E \leq 15 \text{ kV/mm}$, and the power density D_w is preferably in a range of $1 \text{ W/cm}^3 \leq D_w \leq 10 \text{ W/cm}^3$. Further, the decrement rate of the particulate material can be further increased up to approximately 96 % by carrying out the catalytic reaction.

Embodiment III is applicable for decreasing the content of a particulate material contained in an exhaust gas discharged from an automobile, a factory or the like.

According to the above-described process, it is possible to continuously convert a particulate material contained in an exhaust gas from a lean burn engine or the like by the oxidization, to thereby remarkably decrease the content of the particulate material. In addition, this process cannot provide a disadvantage that the exhausting resistance is greatly increased to affect an engine output.